

UNIT 5

CHEMICAL EQUILIBRIUM -I |

Structure

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5.1 INTRODUCTION

Many times, the chemists find that the reaction which they are studying does not go to completion. The concentrations of the reactants and products become somewhat constant. Well, at this point, there seems to be a balance between the opposing reactions and the system is said to be in a condition of equilibrium. We have already dealt in the previous block with the feasibility of the reactions. In this unit we are going to deal with the question, upto what stage does a chemical reaction proceed?

Previously you have learnt that chemical reactions are of two types - irreversible and reversible. The irreversible reactions are those which go to completion. This means that the reaction goes on and on until at least one of the reactants is completely used up. Such reaction proceed in only one direction under a given set of conditions. Whereas those reactions which appear not to proceed beyond a certain stage after sometime even though the reactants are not completely used up are called reversible reactions. They have only reached an equilibrium state. Such reaction can occur in forward as well as backward directions under the same set of conditions. In this unit you will understand the meaning of this state of equilibrium and learn how the

equilibrium composition of the reactants and products are correlated with change in Gibbs energy.

Expected Learning Outcomes

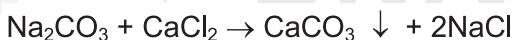
After studying this unit, you should be able to:

- ❖ differentiate between reversible and irreversible reactions;
- ❖ explain chemical equilibrium;
- ❖ derive an expression for equilibrium constant in terms of Gibbs energy; and
- ❖ express the equilibrium constant in different ways.

5.2 REVERSIBLE AND IRREVERSIBLE REACTIONS

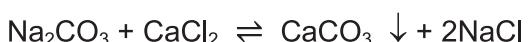
In general, chemical reactions can be divided into two types- reversible and irreversible. Those reactions in which the products can combine back to form the reactants are called reversible reactions. Under usual experimental conditions the irreversible reactions are those where the same reactants cannot be formed back from the products. In this unit, whenever we are referring to reactions in equilibrium, we are referring to reversible reactions.

Now let me narrate to you a short story: Napoleon Bonaparte was the one who helped discover reversible reactions. He brought the concept of reaction reversibility to chemistry. The famous French chemist Claude Louis Berthollet (1748-1822) was appointed as a scientific advisor to him and was taken with him on the most far-flung of his campaigns, even to Egypt in 1798. In Egypt, Berthollet recognized deposits of sodium carbonate around the edges of some of the salt lakes found there. He knew the following reaction



which was known to proceed to completion in the laboratory. Thus he understood that, Na_2CO_3 must have been formed by the reverse of this process brought about by the very high concentration of salt in the slowly-evaporating waters.

Thus it was realized that a chemical reaction such as given above can proceed in both directions – from left to right or vice-versa – depending on the experimental conditions. Each such reaction is usually written containing two half-arrows pointing in opposite directions emphasizing the fact that it is a reversible reaction:



This led Berthollet to question the belief of the time that a reaction could only proceed in a single direction. His famous textbook “*Essai de statique chimique*” (1803) presented his speculations on chemical affinity and his discovery that an excess of the product of a reaction could drive it in the reverse direction.

5.3 CHEMICAL EQUILIBRIUM – A DYNAMIC EQUILIBRIUM

Let us start this unit by recalling when a chemical reaction said to be in equilibrium. As reaction takes place between the reactants, the products are formed and thereby they form a mixture where they are in dynamic equilibrium. As the chemical equilibrium involves a balance between opposite reactions, it is often called dynamic equilibrium. To denote this, a double arrow (\rightleftharpoons) is used between reactants and products.

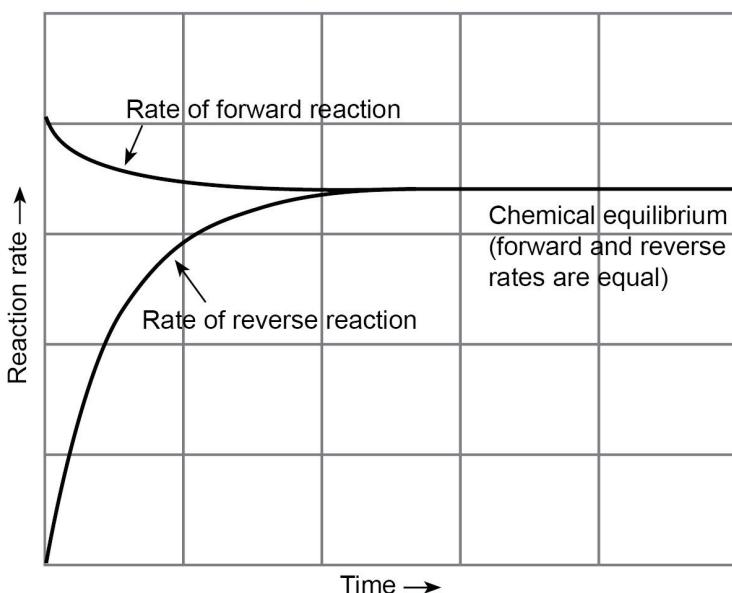


Fig. 5.1: Equilibrium as a dynamic state.

In the above Fig. 5.1 it is shown that, as the reaction reaches the state of equilibrium, reactants form products and products form reactants. This results in a mixture of reactants and products at this stage. At this stage, why you should study this state of equilibrium? Well, it would help us to calculate to what extent the reaction will proceed, the amount of the products formed and the reactants remaining. In the industry, these studies have helped. Industrial processes of importance which are reactions in chemical equilibrium, have been carried out in suitable low-cost conditions so that maximum yield of the desired product can be achieved.

You should note that in such cases where dynamic equilibrium is established, both the forward and reverse reactions occur at the same rate, or speed. You consider any of the components of the chemical reaction as reactants or products. So you see, a chemical reaction can be written in either way. The same may be explained with the following example.

The two equations $H_2 + I_2 \rightarrow 2 HI$ "synthesis of hydrogen iodide", as well as $2 HI \rightarrow H_2 + I_2$ "dissociation of hydrogen iodide" represent the same chemical reaction system in which the roles of the components are reversed, and both yield the same mixture of components when the equilibrium is reached. This is the core concept of chemical equilibrium.

Fig. 5.2 a) and b) below show how the concentrations of the three components of this chemical reaction change with time.

Equi in the word equilibrium means equal. It refers to equal rates of forward and reverse reactions, not to equal quantities or concentrations of the substances involved. The librium part of the word comes from libra, meaning 'balance'. Chemical equilibrium is an equal balance between two reaction rates.

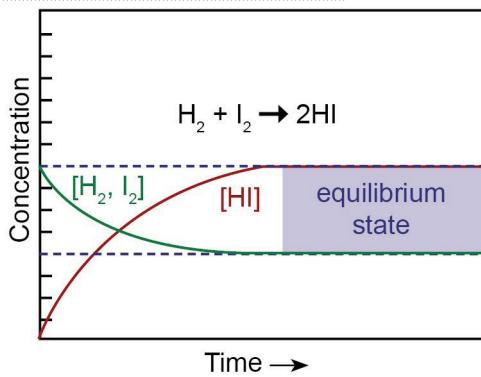


Fig. 5.2 (a)

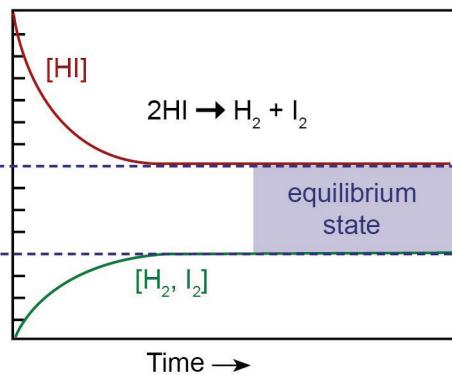


Fig. 5.2 (b)

It does not matter if you start from the left with an equimolar mixture of H_2 and I_2 or you start with a pure sample of hydrogen iodide (Fig. 5.2 b, using twice the initial concentration of HI to keep the number of atoms the same), you will see that whenever equilibrium will be attained (equilibrium state marked on the right) the composition will be the same. So you see that the equilibrium composition does not depend on the direction from which it is approached. Chemical equilibrium is the state reached by a reaction mixture when the rates of forward and reverse reactions have become equal.

For any reaction involving only gases or species in solution (generally aqueous) in which ' a ' moles of substance A react with b moles of substance B to give c moles of substance C and d moles of substance D:



the following holds when equilibrium is established:

$$K_c = \frac{[C]_{\text{eqm}}^c [D]_{\text{eqm}}^d}{[A]_{\text{eqm}}^\alpha [B]_{\text{eqm}}^b} \dots (5.1)$$

where $[A]_{\text{eqm}}$ is the concentration of substance A at equilibrium (mol/L), similarly for substances B, C and D. K_c is called the **equilibrium constant** for the reaction. For a particular reaction, K_c is independent of the initial concentrations, i.e. any combination of concentration of A, B, C and D can be reacted together, yet the same value of K_c is obtained within experimental error. When the respective equilibrium concentrations are inserted into Eq. 5.1 we get the value of K_c . K_c is also called $K_{\text{equilibrium}}$ or simply K .

You may note that the products always appear on the numerator of the expression and the reactants always appear on the denominator. As can be seen from Eq. 5.1, a large value of K_c means that the reaction proceeds extensively from left to right – it may be so large in a particular example that the reaction can be considered to go to completion, e.g., the reaction between an aqueous solution of copper (II) sulphate and iron filings. Conversely a small value of K_c means that very little reaction occurs from left to right.

For reactions that are not at equilibrium, we can write a similar expression called the reaction quotient Q. The reaction quotient (Q) measures the relative amounts of products and reactants present during a reaction at a particular

point in time. With the help of the reaction quotient you can figure out which direction a reaction would proceed, if you are given the concentrations of the reactants and the products. So you can say that if:

- $Q < K$: there is a net conversion of reactants into products as the forward reaction dominates.
- $Q > K$: a net conversion of products into reactants takes place as the reverse reaction dominates.
- $Q = K$ the reaction is in equilibrium: no net change in the composition of the reaction mixture occurs over time.

Table 5.1: Comparison of Q and K Values

Value of Q	What It Means
$Q < K$	Reaction proceeds in forward direction
$Q = K$	Reaction is at equilibrium (\rightleftharpoons)
$Q > K$	Reaction proceeds in reverse direction

The reaction quotient is denoted as Q_c when the concentrations of the reactants and the products are given. Q_c becomes equal to K_c at equilibrium.

The equation for Q_c may be written by multiplying the concentrations for the species of the products and dividing by the concentrations of the reactants. The concentration is raised to the power of the respective stoichiometric coefficients. Q_c therefore is:

$$Q_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \dots(5.2)$$

The Q_c value can be compared to the equilibrium constant, K_c , to determine the direction of the reaction that is taking place. The main difference between K_c and Q_c is that K_c describes a reaction that is at equilibrium, whereas Q_c describes a reaction that is not at equilibrium.

SAQ 1

Can you point out the similarities and dissimilarities of the plot in the Fig. 5.2 (a) and 5.2 (b)?

SAQ 2

Why chemical equilibrium is called a 'dynamic process'?

5.4 GIBBS ENERGY CHANGE IN A CHEMICAL REACTION

In the Unit 4, you have learnt about Gibbs energy. In this section, you will learn about the details of Gibbs energy so that you can arrive at a relationship of it and chemical equilibrium.

In the following Fig. 5.3, Gibbs energy is plotted against the extent of the reaction.

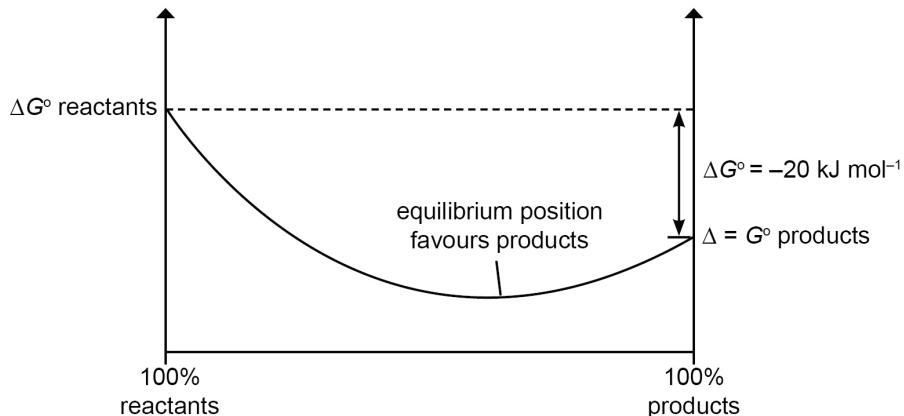


Fig. 5.3: Gibbs energy diagram.

The minimum of the plot in the variations of Gibbs energy as a function of the extent of the reaction (that is how far the reaction has proceeded towards completion), corresponds to the equilibrium composition. This is the way you can find out the equilibrium composition from the minimum of the above plot. Thus, at constant temperature and pressure, the direction of a spontaneous reaction is towards lower values of the Gibbs energy, G .

In the previous unit we learnt how to use the values of ΔG so as to understand whether or not a particular chemical reaction or physical change would be spontaneous under specified conditions. Even if a chemical reaction is spontaneous, it necessarily does not convert all of its reactants to products. So, even if you can say whether a reaction is spontaneous or not, it is not much of use, unless you can also determine just how far the reaction will proceed towards completion. The relationship between ΔG° and the equilibrium constant for the reaction in question can be utilized to determine such things.

Let us study the following chemical reaction:



Equilibrium in this system can be approached from either direction. The question which should arise in your mind now is why does this happen? Now, let us start from the beginning of the above reaction, where we have pure $\text{N}_2\text{O}_4(g)$ and then slowly let the reaction attain equilibrium. As the reaction proceeds, $\text{NO}_2(g)$ molecules start to form, and they mix spontaneously with the remaining $\text{N}_2\text{O}_4(g)$ molecules so that the reaction mixture is homogeneous at all times. In such cases of spontaneous mixing, always there is an associated negative Gibbs energy which is denoted as $\Delta_{\text{mix}}G$. The value of this is negative

at all possible reaction mixture compositions. This signifies that, at any possible reaction mixture composition, the two gases N_2O_4 and NO_2 always mix spontaneously. Thus we can now say that, the total Gibbs energy change for the system is the sum of the Gibbs energy change for the chemical reaction and the Gibbs energy change of mixing.

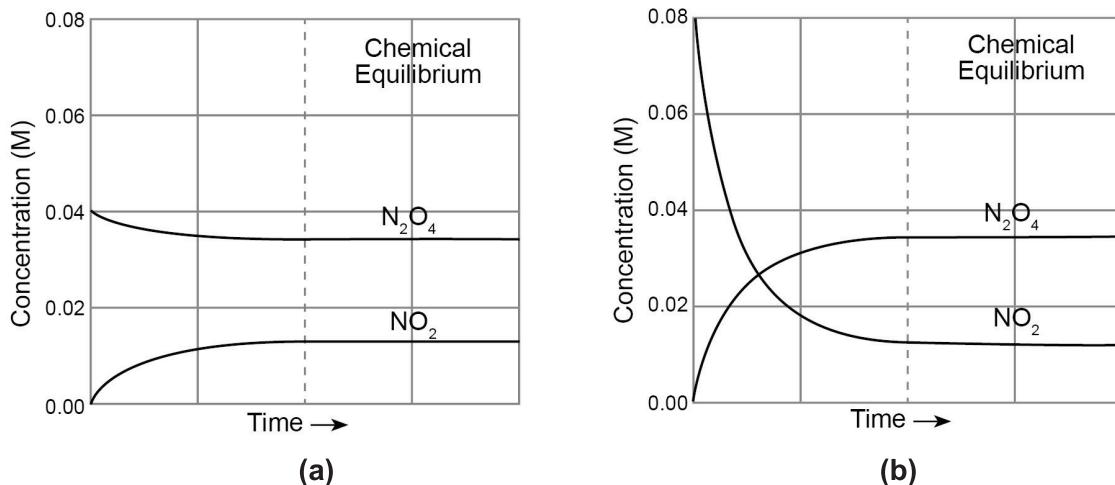


Fig. 5.4: Initial and equilibrium concentrations. Change in the concentrations of N_2O_4 and NO_2 (b) only NO_2 is present initially.

In experiment (a) concentration of NO_2 increases as concentration of N_2O_4 decreases. In experiment (b), concentration of N_2O_4 increases as concentration of NO_2 decreases. In both experiments, a state of chemical equilibrium is reached when the concentrations level off at constant values: $[\text{N}_2\text{O}_4] = 0.0337 \text{ M}$; $[\text{NO}_2] = 0.0125 \text{ M}$. The experiments show that it is a reversible reaction and moves in the direction to achieve and maintain an equilibrium state.

In the Fig. 5.4, rates of the forward and reverse reactions for decomposition of N_2O_4 to NO_2 has been shown. From the plots it is clear that as N_2O_4 is consumed, the rate of the forward reaction decreases; as NO_2 is formed, the rate of the reverse reaction increases. When the two rates become equal, an equilibrium state is attained and there are no further changes in concentrations. At equilibrium, the rates of the forward and reverse reactions are equal.

If the $\text{NO}_2(g)$ molecules formed in the reaction would not have mixed with the $\text{N}_2\text{O}_4(g)$ molecules, then the free energy diagram would simply be a straight line joining $G^0(\text{N}_2\text{O}_4, g)$ and $G^0(\text{NO}_2, g)$ similar to that shown on the Fig. 5.5. However, when we add the contribution from $\Delta_{\text{mix}}G$, we always find that a minimum exists in the Gibbs energy curve. The question is what will be the position of the minimum? Now, that mainly depends on the sign and magnitude of ΔG^0 , the standard Gibbs energy change for the reaction. You must be remembering from the previous unit that $\Delta G = 0$ at equilibrium.

Consider the plot (given in Fig. 5.5) of Gibbs energy, G , versus the number of moles of product (NO_2) formed, which gives the extent of the reaction. On the left side we have pure reactants. On the right side we have pure products.

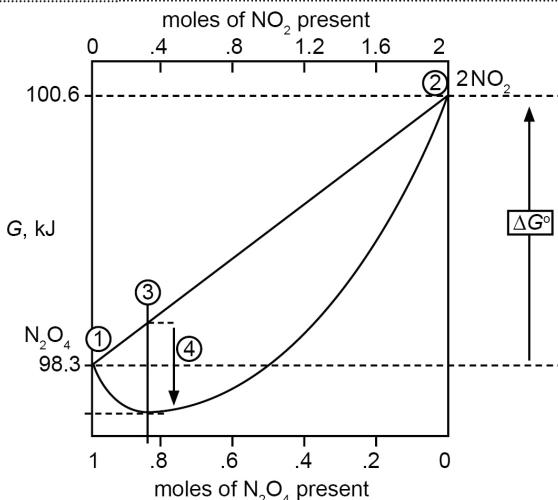


Fig. 5.5: Gibbs energy diagram of N_2O_4 .

At this stage, you can study the plot given in Fig. 5.5. The Gibbs energy of 1 mole of N_2O_4 (1) is smaller than that of 2 moles of NO_2 (2) by 2.3 kJ; thus $\Delta G^\circ = +2.3$ kJ for the complete transformation of reactants into products. The straight diagonal line shows the Gibbs energy of all possible compositions if the two gases were prevented from mixing. The curved line shows the Gibbs energy of the actual reaction mixture. This passes through a minimum at (3) where 0.814 mol of N_2O_4 are in equilibrium with 0.372 mol of NO_2 . The difference (4) corresponds to the Gibbs energy of mixing of reactants and products which always results in an equilibrium mixture whose Gibbs energy is lower than that of either pure reactants or pure products. So some amount of reaction will occur even though ΔG° for the process is positive. From either direction of the curve if you would try to approach the minimum, ΔG for any small change in composition of the reaction mixture starts becoming less negative, until, when you reach the minimum, ΔG for any infinitesimally small change in composition of the reaction mixture becomes zero. Here, the system is at equilibrium. In other words, the value of ΔG for this, and any other reaction, can be found out from the slope of the Gibbs energy diagram. Here you should remember one important point, that is, when the system has a composition corresponding to the minimum in the Gibbs energy diagram, ΔG for any change in composition is positive, thus no change in composition occurs.

5.4.1 Distinction between ΔG and ΔG°

If you closely observe the Fig. 5.5, then you can see that ΔG° for the reaction $\text{N}_2\text{O}_4(g) \rightarrow 2\text{NO}_2(g)$ is positive. At this point you may have this question in mind that, why does the reaction proceed in the forward direction at all. In order to get an answer to this, you must remember that ΔG° is the Gibbs energy change for the conversion of reactants in their standard state to products in their standard state. In this case, the standard state is the pure gases at p° (standard pressure). A sample of $\text{N}_2\text{O}_4(g)$ at p° reacts to give some $\text{NO}_2(g)$. But, the pressure of $\text{NO}_2(g)$ at equilibrium is much less than p° so $\text{N}_2\text{O}_4(g)$ becomes the dominant species in the equilibrium mixture. Next, let us take the example of vapourisation of water, for which ΔG° is $+8.6$ kJ mol^{-1} at 25.0°C . It is well known that water evaporates spontaneously at 25.0°C . What would happen if the value of ΔG° would be positive? It would definitely mean that the partial pressure of water would never reach p° under these

conditions when the system would be at equilibrium. Then what would happen when there is a negative value of ΔG^0 ? All this means that the predominant species at equilibrium would be the products, and also there would be some reactants in the equilibrium mixture. So you can see that from the sign of ΔG^0 one can say about the composition of the reaction mixture at equilibrium.

Another point to be remembered is that ΔG^0 is not a criterion for spontaneity except in the very rare case when the reaction is carried out under standard conditions. You should never forget that the sign of ΔG indicates whether a particular change in composition of the reaction mixture would be spontaneous.

The point 1 in Fig. 5.5 which is 98.3 kJ represents the standard Gibbs energy of the reactants [G^0 (reactants)]. The point 2 in Fig. 5.5 which is 100.6 kJ which represents the standard Gibbs energy of the products [G^0 (products)]. The difference between G^0 (products) and G^0 (reactants) is the standard Gibbs energy change, ΔG^0 .

$$\Delta G^0 = G^0 \text{ (products)} - G^0 \text{ (reactants)}$$

If $\Delta G^0 < 0$, equilibrium shifts to the right, towards products, $K > 1$

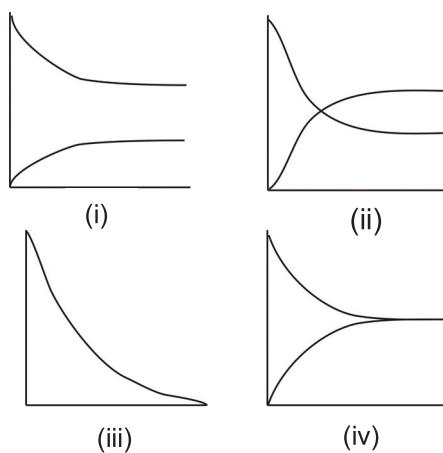
If $\Delta G^0 > 0$, equilibrium shifts to the left, towards reactants, $K < 1$

Wherever the ΔG^0 value for a reaction is too large, 20 kJ or more, and if it is positive, then the reaction may not be observed at room temperature. But you will see that when the reaction after some time under the same conditions achieves completion, then ΔG^0 is both large and negative. Thus, if you inspect the size and sign of ΔG^0 , you will be able to predict whether the spontaneous reaction observed actually occurs.

SAQ 3

Label each graph with the correct description:

- The forward and reverse rates as equilibrium is approached.
- The overall rate as equilibrium is approached.
- The reactant and product concentrations as equilibrium is approached (two graphs)



5.5 CHEMICAL EQUILIBRIUM IN IDEAL GAS MIXTURES: THERMODYNAMIC DERIVATION OF LAW OF CHEMICAL EQUILIBRIUM

If we start with a general reaction



where the reactants A and B form the products C and D. α, b, c and d are their stoichiometric coefficients respectively.

The Chemical potential, μ_i is the change in the Gibbs energy per mole of substance "i" added at constant concentration. The Chemical potential, μ_i of an ideal gas; 'i' in a gaseous mixture is given by

$$\mu_i(p) = \mu_i^0(p) + RT \ln p_i \quad \dots(5.4)$$

where $\mu_i^0(p)$ is the chemical potential of i in the standard state and p_i is its partial pressure.

In earlier units you have studied that the change in Gibbs energy, dG is given by

$$dG = Vdp - SdT \quad \dots(5.5)$$

Again, for the given reaction,

$$\text{Gibbs energy of the products} = c\mu_C + d\mu_D + \dots$$

$$\text{Gibbs energy of the reactants} = \alpha\mu_A + b\mu_B + \dots$$

where μ terms stand for the chemical potential of various substances.

If the values of chemical potential as defined by Eq. 5.4, are substituted for the values of Gibbs energy of products and reactants, then the differences in Gibbs energy, ΔG is given by the following derivation:

At constant temperature ($dT = 0$) and pressure ($dp = 0$), the Gibbs energy change for the above reaction ($\Delta G_{T,P}$) is obtained by using Eq. 5.4 and 5.5.

$$\Delta G_{T,P} = (c\mu_C + d\mu_D + \dots) - (\alpha\mu_A + b\mu_B + \dots) \quad \dots(5.6)$$

where $\mu_C, \mu_D, \mu_A, \mu_B, \dots$, etc. are the chemical potentials of the products and reactants; and α, b, c and d are the stoichiometric coefficients.

Using Eq. 5.4 in Eq.5.6 we get,

$$\begin{aligned} \Delta G_{T,P} &= [c(\mu_C^0(p) + RT \ln p_C) + d(\mu_D^0(p) + RT \ln p_D) + \dots] \\ &\quad - [\alpha(\mu_A^0(p) + RT \ln p_A) + b(\mu_B^0(p) + RT \ln p_B) + \dots] \end{aligned} \quad \dots(5.7)$$

$$\begin{aligned} \Delta G_{T,P} &= [c(\mu_C^0(p) + d(\mu_D^0(p) + \dots) - \alpha(\mu_A^0(p) + b(\mu_B^0(p) + \dots)] \\ &\quad + RT \ln \left[\frac{p_C^c \cdot p_D^d}{p_A^\alpha \cdot p_B^b} \right] \end{aligned} \quad \dots(5.8)$$

Stoichiometric coefficients: is the number written in front of atoms, ions and molecules in a chemical reaction to balance the number of each element on both the reactant and product sides of the equation.

R is the ideal gas constant and in SI unit it's value is $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$.

Note that in the transformation of Eq. 5.7 to Eq. 5.8, we have used the relation:

$$cRT \ln p_C = RT \ln p_C^c$$

i.e. a coefficient (c) of a logarithmic term ($RT \ln p_C$) is taken inside the logarithmic term as a power.

But

$$[c(\mu_C^0(p) + d(\mu_D^0(p))] - [\alpha(\mu_A^0(p) + b(\mu_B^0(p) + \dots)] = \Delta G^\circ_{T,P} \quad \dots(5.9)$$

Where $\Delta G_{T,P}$ is the standard Gibbs energy change of the reaction at constant temperature and pressure.

Using Eqs. 5.8 and 5.9, we can write

$$\Delta G_{T,P} = \Delta G^\circ_{T,P} + RT \ln \left[\frac{p_C^c \cdot p_{D\dots}^d}{p_A^\alpha \cdot p_{B\dots}^b} \right] \quad \dots(5.10)$$

Let us now assume that the above system is under equilibrium. Using Eqs. 5.9 and 5.10, we can write that at equilibrium,

$$\Delta G_{T,P} = \Delta G^\circ_{T,P} + RT \ln \left[\frac{p_C^c \cdot p_{D\dots}^d}{p_A^\alpha \cdot p_{B\dots}^b} \right]_{\text{eq}} = 0 \quad \dots(5.11)$$

The subscript 'eq' stands for equilibrium values of partial pressures.

$$\text{i.e. } \Delta G^\circ_{T,P} = -RT \ln \left[\frac{p_C^c \cdot p_{D\dots}^d}{p_A^\alpha \cdot p_{B\dots}^b} \right]_{\text{eq}} \quad \dots(5.12)$$

$$\text{or } \Delta G^\circ_{T,P} = -RT \ln K_p = -2.303 RT \log K_p \quad \dots(5.13)$$

Where K_p is the equilibrium constant in terms of partial pressures.

Now let us look at the following problems which are given as examples.

Example 5.1:

- a) In a reversible reaction which reaches equilibrium, when will ΔG° be equal to zero?

Solution

$$\Delta G^\circ = -RT \ln K$$

If $K = 1$, $\ln K = 0$ and $\Delta G^\circ = 0$, i.e. ΔG° will be zero when K is unity.

- b) When will ΔG° be negative for an equilibrium reaction?

Solution

$$\Delta G^\circ = -RT \ln K \text{ (at equilibrium)}$$

Since RT is positive, ΔG° will be negative only when $\ln K$ is positive; $\ln K$ will be positive quantity only when the value of K is greater than unity.

- c) When will ΔG° be positive?

Solution

If you follow the statements made in b), then you will obviously be able to conclude that ΔG° will be positive only when K is less than unity.

- d) Estimate K at 300 K when ΔG° is 1350 cal mol⁻¹.

Solution

SI unit of energy is joule (J) and 1 calories is equal to 4.1858 Joule.

$$\Delta G^\circ_{300} = -R \times 300 \ln K$$

$$\ln K = -\Delta G^\circ_{300}/R \times 300$$

$$\log K = -(1350 \times 4.1858)/(8.314 \times 300 \times 2.303) = -0.9837$$

or $K = 0.1038$

Try the following SAQs which is based on the above discussion.

SAQ 4

At 298.15 K, the ΔG° for the dissociation of acetic acid,



is 27.2 kJ mol⁻¹. Calculate the equilibrium constant for the above reaction.

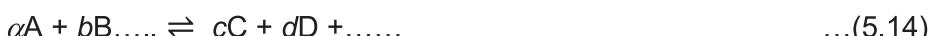
5.6 EQUILIBRIUM CONSTANTS – K_p , K_c , K_x

In this section we are going to study the equilibrium constants for reactions which are not only studied in gaseous system but may be in solutions also. So here you must remember a very important point. For such case, the K is to be expressed in the appropriate concentration units. The symbols K_p , K_c , K_x are generally used to signify that the equilibrium constant expression contains partial pressures, molar concentrations or mole fractions respectively.

5.6.1 K_p

For reactions involving gases, it is convenient to express concentration of any gas at any given temperature in terms of its partial pressure.

To define equilibrium constant in terms of the partial pressures of the reactants and products, you should consider the general gaseous reaction,



Where p_A , p_B , p_C , p_D , ..., etc., are the partial pressures of A, B, C, D, ..., etc., at equilibrium and α , b , c and d are their stoichiometric coefficients, the equilibrium constant may be written as,

$$K_p = \frac{p_C^c \cdot p_D^d \dots}{p_A^\alpha \cdot p_B^b \dots} \quad \dots(5.15)$$

where K_p is the equilibrium constant in terms of partial pressure and is a constant at a given temperature. It should be noticed that Eq. (5.15) is valid for a system involving ideal gases.

So at equilibrium,

$$\Delta G^\circ_{T,P} = -RT \ln K_p = -2.303 RT \log K_p \quad \dots(5.16)$$

where K_p is the equilibrium constant in terms of partial pressures. The relationship is known as van't Hoff isotherm.

Eq. 5.15 can also be written as,

$$K_p = p_C^c \cdot p_D^d \cdot p_A^{-\alpha} \cdot p_B^{-b} \quad \dots(5.17)$$

Again, from Eqs. 5.15 to 5.17, we can see that the dimensions of K_p will depend upon the stoichiometric coefficients of the reactants and products.

This particular aspect will be clear when you study the examples worked out in this unit.

Let us illustrate the use of Eq. 5.15 with an example.

Example 5.2: Suppose that, in an experiment $2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g)$

at 1000 K, it is found that

$$p_{\text{SO}_2} = 3.42 \times 10^4 \text{ Pa}, \quad p_{\text{O}_2} = 3.13 \times 10^4 \text{ Pa} \text{ and}$$

$$p_{\text{SO}_3} = 3.58 \times 10^4 \text{ Pa} \text{ for the reaction.}$$

Calculate the value for the equilibrium constant K_p .

Solution: At the given temperature, K_p is given by the expression

$$K_p = (p_{\text{SO}_3})^2 \cdot (p_{\text{SO}_2})^{-2} (p_{\text{O}_2})^{-1}$$

$$\text{or} \quad K_p = \frac{(p_{\text{SO}_3})^2}{(p_{\text{SO}_2})^2 \cdot (p_{\text{O}_2})}$$

$$= \frac{(3.58 \times 10^4 \text{ Pa})^2}{(3.42 \times 10^4 \text{ Pa})^2 \times (3.13 \times 10^4 \text{ Pa})} = 0.35 \times 10^{-4} \text{ Pa}^{-1}$$

Try the following SAQ now.

SAQ 5

Suppose that we write the ammonia synthesis reaction in two different ways:

- i) $\frac{1}{2} \text{N}_2(g) + \frac{3}{2} \text{H}_2(g) \rightleftharpoons \text{NH}_3(g)$ and ii) $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$

Would you expect any difference in the expression for K_p in the two cases?

(Usually, K_p values are calculated using equations of the type (ii) which have integral stoichiometric coefficients).

5.6.2 K_c

The constant K_c is known as the *equilibrium constant* of the particular reaction and gives the ratio of the concentrations of the products to the concentrations of the reactants. The subscript c indicates that the equilibrium condition is expressed in terms of the concentration units, i.e., moles per litre of the various species.

K_c is thus given by the expression,

$$= \frac{c_C^c \cdot c_D^d}{c_A^\alpha \cdot c_B^\beta \dots} \quad \dots(5.18)$$

where c is the molar concentration.

5.6.3 K_x

K_x is defined by,

$$= \frac{x_C^c \cdot x_D^d}{x_A^\alpha \cdot x_B^\beta \dots} \quad \dots(5.19)$$

where, x_i = mole fraction of the species i.

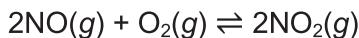
Since Dalton's law tells us that partial pressure of a gas is equal to the mole fraction times the total pressure, we can write $p_i = x_i p_t$, where p_i is the partial pressure of the i^{th} species. So, Eq. 5.19 can be written as,

$$K_x = (x_C p_t)^c \cdot (x_D p_t)^d \dots (x_A p_t)^{-\alpha} (x_B p_t)^{-\beta} \quad \dots(5.20)$$

where, x_i = mole fraction of the species i, and p_t = total pressure

SAQ 6

Express the equilibrium constant K_p for the reaction,



According to Dalton's law of partial pressure, partial pressure (p_i) of an ideal gas, i, is given by,

$$p_i = p_t x_i$$

where p_t is the total pressure, and x_i is the mole fraction of the gas in a gaseous mixture.

In terms of (i) partial pressures and (ii) mole fractions of the gaseous species.

5.7 RELATION BETWEEN – K_p , K_x , K_c

5.7.1 Relation between K_p and K_c

The values of K_p and K_c for a given reaction is not same. The relationship between these constants can be obtained at a particular temperature when we are dealing with ideal gases. For any ideal gas, the pressure is given by

$$P = \left(\frac{n}{V} \right) RT \quad \dots(5.21)$$

where V is the volume occupied by n moles of gas at temperature T .

You must be knowing that $\frac{n}{V}$ is nothing else but the molar concentration c ,

therefore

$$p_i = \frac{n_i RT}{V} = c_i RT \quad \dots(5.22)$$

where c_i is the molar concentration of the i^{th} species.

Substituting this value of P in Eq. 5.15 we get,

$$\begin{aligned} K_p &= \frac{(c_C RT)^c \cdot (c_D RT)^d \dots}{(c_A RT)^\alpha (c_B RT)^\beta \dots} \\ &= \frac{c_C^c \cdot c_D^d \dots}{c_A^\alpha c_B^\beta \dots} (RT)^{(c+d+\dots)-(\alpha+\beta+\dots)} \end{aligned} \quad \dots(5.23)$$

Now, $K_c = \frac{c_C^c \cdot c_D^d \dots}{c_A^\alpha c_B^\beta \dots}$

Thus, $K_p = K_c (RT)^{\Delta n} \quad \dots(5.24)$

where Δn = number of moles of gaseous products - number of moles of gaseous reactants

If $\Delta n = 0$, then number of moles of reactants is the same as the number of moles of products in gaseous phase.

Then, $K_p = K_c$

5.7.2 Relation between K_p and K_x

You have already derived the relation for K_p in Eq. 5.12 to 5.15. Now in this section let us start with the relation in Eq. 5.15:

$$K_p = \left[\frac{p_C^c \cdot p_D^d \dots}{p_A^\alpha \cdot p_B^\beta \dots} \right]$$

Now, you know that, in a gaseous mixture, the partial pressure of the component A, p_A , its mole fraction, x_A , and the total pressure P are related as

$$p_A = x_A P \quad \dots(5.25)$$

Similarly $p_B = x_B P$; $p_C = x_C P$ and $p_D = x_D P$

Substituting the values in Eq.5.15, we get

$$\begin{aligned} K_p &= \frac{(x_C P)^c \cdot (x_D P)^d \dots}{(x_A P)^\alpha \cdot (x_B P)^\beta \dots} \\ &= \frac{(x_C)^c \cdot (x_D)^d \dots}{(x_A)^\alpha \cdot (x_B)^\beta \dots} (P)^{(c+d+\dots)-(\alpha+\beta+\dots)} \end{aligned} \quad \dots(5.26)$$

In Eq. 5.26

$$\frac{(x_C)^c \cdot (x_D)^d \cdots}{(x_A)^\alpha \cdot (x_B)^\beta \cdots} = K_x$$

So, you can say that,

$$K_p = K_x (P)^{(c+d+\dots) - (\alpha+\beta+\dots)} = K_x (P)^{\Delta n} \quad \dots(5.27)$$

You should note here that K_c and K_p depend on temperature, but K_x depends on total pressure and temperature.

With the help of the following example you will be able to understand clearly the relation between K_p and K_x .

Example 5.3:

Now, with the help of this example you will understand, how the equilibrium constant depends on the form of the chemical equation:

The equilibrium between hydrogen, nitrogen, and ammonia can be written in the more than one way:

- (i) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
- (ii) $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$
- (iii) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$

If the value of equilibrium constant for the first reaction is given as 0.19 at 532°C.

Write the equilibrium constant expression and calculate its value for the other two reactions at the same temperature.

The strategy that you should follow is:

First, corresponding to each equation write the equilibrium constant expression, then examine the concentration terms to determine the relationship between equilibrium expressions. Then utilize these relationships to calculate the relationships between equilibrium constants.

Solution

The expressions for the equilibrium constants are:

$$K_1 = \frac{[NH_3]^2}{[N_2][H_2]^3} = 0.19$$

$$K_2 = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}}$$

$$K_3 = \frac{[N_2][H_2]^3}{[NH_3]^2}$$

If you look at the concentration terms in the expressions for K_1 and K_2 then you will see that,

$$K_2 = \left\{ \frac{[\text{NH}_3]}{[\text{N}_2]^{1/2} [\text{H}_2]^{3/2}} \right\}$$

$$K_1 = (K_2)^2$$

Now, check this equation by squaring each term in the equilibrium constant expression for K_2 and then verify that $(K_2)^2$ is equal to K_1 . So you can say,

$$(K_2)^2 = K_1 = 0.19$$

To calculate K_2 , take the square root:

$$K_2 = 0.44$$

Thus, we can say that when the stoichiometry is halved, the new K is the square root (1/2 power) of the old K .

The third equation is the reverse of the first, so the new K_3 is the old K_1 raised to the -1 power.

$$K_3 = (K_1)^{-1} = \frac{1}{K_1} = \frac{1}{0.19}$$

$$K_3 = 5.3$$

Thus you can see that the values of K have been validated and provide equivalent information. Each value of K thus can be applied to a specific form of equation.

Example 5.4:

Consider the equilibrium



If the numerical value of K_p is 0.68 at 458 K, calculate K_c .

Methodology to be followed: Compute Δn from the chemical equation, then use the relationship $K_p = K_c(RT)^{\Delta n}$ to solve K_c . ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ and temperature in Kelvin).

Solution : You should first calculate Δn . There are 2 mol of gas on the product side of the chemical equation, and there is 1 mol of gaseous reactant, so Δn is +1 in this case. From $K_p = K_c(RT)^{\Delta n}$, you can say

$$K_c = \frac{K_p}{(RT)^{\Delta n}}$$

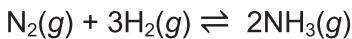
After substituting the numerical values for K_p , R , T and Δn in the equation,

$$K_c = \frac{0.68}{(8.314 \times 458)^{+1}}$$

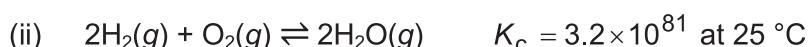
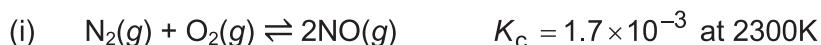
$$K_c = 1.79 \times 10^{-4}$$

SAQ 7

K_p for the formation of 2 mol ammonia from nitrogen and hydrogen is 2.8×10^{-9} at 298 K. Calculate K_c for

**SAQ 8**

For the reactions given below, calculate K_p from K_c .



5.8 SUMMARY

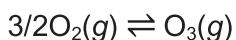
In this unit, we have discussed the meaning of reversible and irreversible reactions as well as chemical equilibrium. A general expression for the equilibrium constant was derived from the basic principles of thermodynamics. The various types of equilibrium constants K_p , K_c and K_x as well as their relation were also discussed.

5.9 TERMINAL QUESTIONS

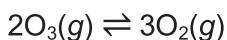
1. In a reaction $\text{A} + 2\text{B} \rightleftharpoons 2\text{C} + \text{D}$, A and B are taken in a closed vessel at 300 K. The initial concentration of B is 1.5 times that of A. At equilibrium, the concentration of A and D are equal. Calculate the equilibrium constant at 300 K.
2. Write an equilibrium constant expression for each chemical equation:
 - a) $4\text{NO}_2(g) + \text{O}_2(g) + 2\text{H}_2\text{O}(g) \rightleftharpoons 4\text{HNO}_3(g)$
 - b) $\text{CH}_4(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + 3\text{H}_2(g)$
3. The balanced equation for conversion of oxygen to ozone has a very small value of K_c .



- a) What is the value of K_c if the equation is written as?



- b) What is the value of K_c for the conversion of ozone to oxygen?



4. In the equilibrium mixture of three ideal gases A, B, C, $\text{A}(g) \rightleftharpoons \text{B}(g) + \text{C}(g)$ obtained by dissociation of A to the extent of 20% at a total pressure of 1.0 atm, what are the partial pressures of A, B and C?

5. Calculate the equilibrium constant of a reaction at 300 K if ΔG° at this temperature for the reaction is 29.29 kJ mol⁻¹.
6. If an equilibrium is product-favoured, is its equilibrium constant large or small with respect to 1? Explain.

5.10 ANSWERS

Self-Assessment Questions

1. Similarities: final (equilibrium) concentrations of the components are the same in the two cases.

Dissimilarities:

In a) the concentration of product is zero initially

In b) the concentration of reactant is zero initially.

2. Chemical equilibrium is the state reached by a reaction mixture when the rates of forward and reverse reactions have become equal. If the reaction is studied it can be seen that there is no net change, although the forward and reverse reactions continue. Since both the forward and the reverse reactions are continuing so the equilibrium is a 'dynamic' process.

3. a) (i)
- b) (iii)
- c) (ii) and (iv)

4. $\log K = -\Delta G^\circ / 2.303 RT$

$$= -27.2 \times 1000 \text{ Jmol}^{-1} / (2.303 \times 8.314 \times 298.15 \text{ Jmol}^{-1})$$

$$K = 1.72 \times 10^{-5}$$

5. No there would be no differences in the expressions in the two cases.

6. (i) $K_p = \left[\frac{p_{\text{NO}_2}^2}{p_{\text{NO}}^2 \cdot p_{\text{O}_2}} \right]$

$$K_x = \frac{x_{\text{NO}_2}^2}{x_{\text{NO}}^2 x_{\text{O}_2}}$$

7. $K_c = 1.7 \times 10^{-2}$

8. (i) $K_p = K_c (RT)^{\Delta n} = 1.7 \times 10^{-3} (RT)^0 = 1.7 \times 10^{-3}$

- (ii)
$$\begin{aligned} K_p &= K_c (RT)^{\Delta n} = 3.2 \times 10^{81} (RT)^{-1} = 3.2 \times 10^{81} (8.314 \times 298)^{-1} \\ &= 1.29 \times 10^{78} \end{aligned}$$

Terminal Questions



Initial	a	$1.5a$	0	0
Equilibrium	$a-x$	$1.5a-2x$	$2x$	x

Now, $a - x = x$, so $a = 2x$

$$1.5a - 2x = 3x - 2x = x$$

So,

$$K = \frac{[C]^2[D]}{[A][B]^2} = \frac{\left(\frac{2x}{V}\right)^2 \left(\frac{x}{V}\right)}{\left(\frac{x}{V}\right) \left(\frac{x}{V}\right)^2} = 4$$

2. a) $K_c = \frac{[\text{HNO}_3]_{\text{eqm}}^4}{[\text{NO}_2]_{\text{eqm}}^4 [\text{O}_2]_{\text{eqm}} [\text{H}_2\text{O}]_{\text{eqm}}^2}$

b) $K_c = \frac{[\text{CO}]_{\text{eqm}} [\text{H}_2]_{\text{eqm}}^3}{[\text{CH}_4]_{\text{eqm}} [\text{H}_2\text{O}]_{\text{eqm}}}$

3. a) When the stoichiometric coefficients are changed by multiplying by the factor half on both sides:

$$\begin{aligned} K_{c_{1/2}} &= \frac{[\text{O}_3]_{\text{eqm}}}{[\text{O}_2]_{\text{eqm}}^{3/2}} = \left[\frac{[\text{O}_3]_{\text{eqm}}^2}{[\text{O}_2]_{\text{eqm}}^3} \right]^{1/2} = (K_c)^{1/2} \\ &= (6.25 \times 10^{-58})^{1/2} \\ &= 2.5 \times 10^{-29} \end{aligned}$$

- b) For the reverse reaction the equilibrium constant becomes the inverse of the original one, that is 1.6×10^{57} .

4. Let us take one mole of A to start with. Since 20% of A is dissociated, the equilibrium amounts of A, B, C according to the reaction $\text{A} \rightleftharpoons \text{B} + \text{C}$ will be $n_A = 1 - 0.2 = 0.8$ mole; $n_B = 0.2$ mole and $n_C = 0.2$ mole

$$\text{Total number of moles } N = n_A + n_B + n_C = 0.8 + 0.2 + 0.2 = 1.2$$

∴ Mole fractions of A, B, C at equilibrium are:

$$x_A = \frac{0.8}{1.2}; \quad x_B = \frac{0.2}{1.2}; \quad x_C = \frac{0.2}{1.2}$$

Total pressure P (from the data) = 1 atm.

and Partial pressure $p = \text{Total pressure} \times \text{mole fraction}$

$$\therefore \text{Partial pressure of A, } p_A = \frac{0.8}{1.2} \times 1.0 = 0.667 \text{ atm.}$$

Similarly $p_B = \frac{0.2}{1.2} \times 1.0 = 0.167 \text{ atm.}$

and $p_C = \frac{0.2}{1.2} \times 1.0 = 0.167 \text{ atm.}$

- Substituting the values of

$$\Delta G^\circ = 29.29 \times 10^3 \text{ Jmol}^{-1} = 29290 \text{ Jmol}^{-1};$$

$$T = 300 \text{ K}$$

$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \text{ in the equation}$$

$$\Delta G^\circ = -RT \ln K$$

we get

$$29290 = -8.314 \times 300 \times 2.303 \log K$$

$$\Rightarrow \log K = -\frac{29290}{8.314 \times 300 \times 2.303} = -5.0991$$

$$\text{Whence } \Rightarrow K = 7.96 \times 10^{-6}.$$

- Equilibrium constants are used to predict whether a reaction will favour the products or the reactants. If $K > 1$, the reaction will be product-favoured.